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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Paper

We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved paper. It more particularly relates to an improved paper containing small particles of a synthetic thermoplastic polymer.

Paper has many uses in packaging, printing, and preparation of containers. One of the basic shortcomings of conventional paper is its weight. The high density of paper imposes a significant financial burden in shipping or mailing. For example, magazines, when printed on a paper which is sufficiently dense and thick to give the reader the impression of quality, weighs considerably more than is necessary if the minimum thickness of paper were used which would permit readability. Frequently among the thicker papers, often referred to as paperboard or boxboard, a high weight is required to obtain a desired thickness and stiffness. In many instances, such as in the preparation of paper cups, present papers do not have a sufficient insulating value for use as cups for hot liquids unless an excessive quantity of pulp is employed.

In accordance with the present invention improved paper has now been made available having improved opacity, stiffness and insulating properties and significantly reduced density without substantial loss in tear-resistance and bursting strength. The improved paper of the invention is comprised of a non-woven web of fibers containing enmeshed therein a plurality of synthetic thermoplastic polymer particles each of which is a substantially spherical, hollow particle, preferably in a proportion of from 0.05 to 60 percent of the weight of fibres in the paper. The thickness of the web and the coarseness or fineness of the pulp fibers will more or less limit the size of the hollow particles which may be enmeshed in the web. It is generally desirable for the hollow particles to have a diameter from 0.5 to 200 microns. Preferably, the hollow particles are between 3 and 50 microns in diameter. Substantially any hollow synthetic thermoplastic polymer particle of such size may be enmeshed in a paper web; however, hollow methyl methacrylate polymer particles are preferred.

The invention also relates to a process of making paper comprised of depositing a plurality of fibers upon a screen from an aqueous suspension and subsequently drying and compressing the deposited fibers to form a generally continuous non-woven web. As an essential feature of the process, the aqueous suspension from which the fibers are deposited contains a plurality of substantially spherical, hollow synthetic thermoplastic polymer particles dispersed therein. Advantageously the aqueous suspension contains a dispersing agent to promote the dispersion of the hollow particles.

Preferably the hollow polymer particles have bulk densities from 0.2 to 3 pounds per cubic foot (3.2 to 48 grams per liter). Such small hollow particles may be prepared by suspension polymerization of a polymerizable monomer and a volatile blowing agent and heating the particulate polymer to expand the volatile blowing agent.

In a typical process, a polymerization reactor was equipped with an agitator and charged with 100 parts of deionized water and 15 parts of a 30 weight percent colloidal silica

Price

dispersion in water. To this mixture was added 2.5 parts of a 10 weight percent aqueous solution of a copolymer prepared from diethanolamine and adipic acid in equimolar proportions by carrying out a condensation reaction to give a product having a viscosity of about 100 centipoises at 25°C. One part of a solution containing 2.5 weight percent potassium dichromate was added. The pH of the aqueous solution was adjusted to 4 with hydrochloric acid. Methyl methacrylate was utilized as the monomer. An oil-phase mixture was prepared utilizing 100 parts of methyl methacrylate and containing 20 weight percent neopentane (27.6 volume-percent based on the total volume of the monomer-neopentane mixture) and 0.1 part of benzoyl peroxide as a catalyst. The oil-phase mixture was added to the water phase with violent agitation supplied by a blade rotating at a speed of about 10,000 rpm. The reactor was immediately sealed and a portion sampled to determine the particle size. The droplets appeared to have diameters of from 2 to 10 microns. After the initial dispersion, the reaction mixture was maintained at a temperature of 80°C. for a period of 24 hours. At the end of this period, the temperature was lowered and the reaction mixture had the appearance of a white, milky liquid. A portion of the mixture was filtered and the polymer particles subsequently dried in an air oven at a temperature of 30°C. A portion of the dried spherical particles were heated in an air oven at a temperature of 150°C. for 3 minutes. Upon heating, the particles showed a marked increase in volume. Microscopic examination of the particles prior to foaming indicated particles having diameters of from 2 to 10 microns and each having disposed therein a distinct spherical zone which appeared to contain liquid and a small vapor space. The particles which had been heated were examined microscopically and were found to have diameters of from 2 to 5 times the diameter of the original particle I.E. 4 to 50 microns, and to have a relatively thin, transparent wall and a gaseous center, i.e. a monocell.

The hollow spherical particles are readily incorporated into a paper pulp by mixture with the wet pulp prior to deposition on the Fourdrinier screen or on the collecting surface of a cylinder machine. Depending upon the particular surface characteristics of the hollow particle, it may be necessary to incorporate a coagulant or retention aid into the pulp slurry to assure that a major proportion of the plastic particles is deposited on the surface of the pulp fibers and is not carried away by the white water. Generally the hollow particles are utilized in a paper in concentrations of from 0.05—60 percent by weight depending upon the desired characteristics of the resultant paper. If papers of minimum bulk density are desired, a maximum quantity of particles is incorporated therein. If maximum physical strength is desired, generally a smaller proportion is used. Beneficially the incorporation of from 5—15 percent by weight of such particles is oftentimes sufficient to reduce the density of a paper sufficiently to provide a significant decrease in the cost of mailing of a finished printed article such as a magazine or a book. Yet all of the required physical characteristics of the paper are retained. The hollow particles or microspheres employed in the present invention are readily incorporated in either long-fiber or short-fiber pulps, and also in groundwood pulps and rag pulps. The incorporation of the polymer particles provides on an equal-basis-weight comparison a significant increase in the stiffness of the paper as well as a significant increase in the caliper. Thus, it makes possible the preparation of papers having greater stiffness, lighter weight, and increased caliper, all desirable features for many books and magazines.

The following experiments serve to illustrate the benefits and advantages of the present invention and employ the following terms:

Freeness of pulp is a measure of the rate of flow of water through the pulp and is measured in accordance with the TAPPI Standard T227 m-58, also referred to as the Canadian Standard Freeness.

Stiffness of the paper or sheets is measured in accordance with the TAPPI Standard T489 m-60 also known as Taber stiffness. Ring crush refers to the Ring crush test of paperboard in accordance with the TAPPI Standard T472 m-51. The Pick test is designed to test the surface strength of paper and is performed in accordance with TAPPI Standard T459 m-48.

The equipment employed for forming hand sheets was generally in accord with that described in the TAPPI Standard "Forming Hand Sheets for Physical Tests of Pulp" T205 m-58. Hand sheets were prepared by beating the pulp to the desired freeness and subsequently adding to the paper furnish the hollow polymer particles and an adhesive as retention aid and transferring the slurry to the deckel box and subsequently draining the water from the deckel box after any obvious movement of the slurry had ceased. The hand sheet was formed on an 80-mesh (31 wires per cm) screen and subsequently dried by the following procedure. The hand sheet and screen are removed from the deckel box, the sheet pressed against and transferred to a sheet of blotting paper. The sheet was then placed against a polished chromium-plated sheet under a pressure of 50 pounds per square inch (3.5 kg/cm^2) for a sufficient length of time to remove by capillary action the majority of water available thereto. The sheet of blotting paper is removed and replaced with a half-inch (12.7 mm.) felt. The felt-paper-plated-sheet sandwich is placed in a platen press between closed

platens for a period of 4 minutes. The platen adjacent to the plated sheet was heated to a temperature of 115°C. The hand sheet was then removed from the press and sandwich and conditioned for 24 hours at a temperature of 73°C. under a relative humidity of 50 percent before testing.

Opacity is measured in accordance with TAPPI Standard T425 m-60 with the exception that a wave length of 560 millimicrons was used. The breaking length is the length in meters of a sheet of paper sufficient to cause the paper to rupture under its own weight. The M.I.T. fold was determined in accordance with TAPPI Standard T423 m-50.

The experimental data obtained from the experiments are set forth in the following tables wherein the microspheres (M) are the methyl methacrylate polymer spheres prepared in the manner herinbefore described, and having average diameters from 5 to 50 microns.

TABLE I

	Control		*A+10% Microspheres(M)		**Cato 8+10% Microspheres(M)	
			0.5% A*	0.75% A*	1% Cato 8	3% Cato 8
Basis Weight, gm/m²	70.3	57.6	57.6	57.6	57.6	57.6
Microspheres Retained Weight %	—	—	3.0	2.9	3.7	4.1
Bulk, cc/gm	1.28	1.38	1.56	1.62	1.55	1.57
Caliper in inches	0.0035	0.0031	0.0037	0.0038	0.0038	0.0039
TAPPI Opacity %	86.8	78.8	87.6	89.2	88.6	88.9
Brightness, R	0.627	0.620	0.689	0.691	0.689	0.688
Burst Factor ***	35.8	30.3	28.7	26.8	27.6	27.8
Tensile breaking length	6330	6560	6130	5750	6090	6400
Tensile, p.s.i.	6400	6350	5390	4770	5150	5460
Tear factor****	69.7	48.5	60.7	56.8	54.9	62.5
M.I.T. Fold	27	35	64	90	73	280

*A A synthetic polymeric adhesive employed as a retention aid and added to the pulp slurry to assure that a major proportion of the plastic particles is deposited on the surface of the pulp fibres.

** Cato 8 A cationic starch manufactured by National Starch Company

*** Burst factor from TAPPI Standard T403 m—53 $= \dfrac{\text{bursting strength gms/cm}^2}{\text{basis weight gms/m}^2}$

**** Tear factor from TAPPI Standard T414 m—49 $= \dfrac{\text{Tearing resistance gms}}{\text{Basis Weight gms/m}^2} \times 100$

psi = pounds per square inch

TABLE II

	Blank	+3% Alum**	+3% Alum +10% Microspheres	10% Microspheres and 3% Alum + *Mydel 550	
				0.5% Mydel 550	0.75% Mydel 550
Basis weight, g/m²	70.3	57.6	57.6	57.6	57.6
% Microspheres Retained	—	—	3.1	3.7	4.3
Bulk, cc/gm	1.31	1.40	1.61	1.61	1.64
Caliper in inches	0.0036	0.0032	0.0037	0.0039	0.0040
TAPPI Opacity %	86.4	79.2	86.8	87.8	87.8
Brightness, R	0.638	0.630	0.688	0.697	0.697
Burst Factor	34.9	26.1	23.5	31.5	26.7
Breaking length	6340	6580	5570	5830	6100
Tensile, p.s.i.	6400	6400	4530	4820	4850
Tear Factor	68.4	49.9	63.5	54.1	56.9

* Mydel 550 Trademark for a copolymer of acrylamide and acrylic acid

** Aluminum sulphate $Al_2(SO_4)_3 18H_2O$

Paper containing small hollow thermoplastic polymer microspheres was prepared on an experimental paper machine of the Fourdrinier type utilizing the following material. The furnish or solids in the pulp slurry comprises 50 percent by weight unbleached groundwood pulp, 35 percent by weight bleached sulfite pulp and 15 percent by weight bleached kraft. The furnish was beaten to a Canadian Standard freeness of 300 milliliters. After beating one-half of one percent by weight based on the dry weight of the furnish of a rosin size was added. The pH of the resultant slurry was 6.2 which was subsequently adjusted to 4.5 by means of sulphuric acid in the stock and machine chests. During operation, the pH at the fan pump varied between 5.1 and 5.5 A slurry in water of hollow polymer particles having a dimeter of from 7 microns to 110 microns was prepared and metered into the recycle water going to the fan pump. The paper machine was placed in operation without the addition of the hollow polymer particles. After operating for a period of time the quantity of polymer spheres added to the stock was varied. The results are set forth in the following tables. For comparative purposes calculations have been made to provide values for constant basis weight paper having the value of 41.6 g/sq.m.

TABLE III

	Initial Control	Microspheres Added				O Final Control
		2.7%	4.6%	10.2%	12.1%	
Microspheres** (by Pyrolysis) wt. %	0	0.5	1.1	1.7	2.3	0
Bulk cc/gm (average)	2.30	2.48	2.52	2.65	2.71	2.33
Dry Burst Factor	7.2	6.9	6.1	5.8	5.4	7.0
TAPPI Opacity %	76.2	77.5	76.7	78.7	78.2	76.1
Brightness R ∞	.712	.719	.721	.724	.724	.718
Tensile, breaking length — machine direction	2900	3000	2600	2400	2200	3100
Tensile, breaking length — cross machine direction	2200	2200	2100	1900	1800	2000
Tear Factor — machine direction	45	45	47	46	44	47
Tear Factor — cross machine direction	47	47	49	49	45	47
M.I.T. Fold (0.5 Kg.) — machine direction	38	31	23	20	15	41
M.I.T. Fold (0.5 Kg.) — cross machine direction	22	17	14	13	14	13
Tensile lbs/sq. in. — machine direction	1700	1700	1500	1300	1100	1900
Tensile lbs/sq. in. — cross machine direction	1300	1200	1200	1000	900	1200

** methyl methacrylate microspheres of 7 to 107 microns averaging 20 microns in diameter and a density of 3.9 pounds per cubic foot.

By way of further illustration, several hand sheets were prepared in a manner hereinbefore described utilising a 1:1 mixture of bleached ground wood pulp and an unbleached spruce sulfite pulp beaten to a Canadian Standard freeness of 157 milliliters; the hand sheets were made up to a basis weight of about 120 grams per square meter. Three percent by weight of alum based on the weight of the pulp was added and the pH adjusted to 5.2 by means of N/10 NaOH.

Numerous batches of microballoons have been prepared from methyl methacrylate by the method hereinbefore described. Data shown in Tables IV and V were obtained on a batch (34 CR8) having a density of 4.3 pounds per cubic foot (68.8 gm/l) and average diameters of 10 microns and on another batch (579) having a density of 0.6 pound per cubic foot (9.6 gm/l) and average diameters of 20 microns.

In a manner similar to the foregoing illustrations other papers having generally commensurate benefits are prepared which contain expanded hollow synthetic thermo-plastic polymer particles of a copolymer of 80 weight percent methyl methacrylate, and 20 weight percent styrene; a copolymer of 90 weight percent methyl methacrylate and 10 weight percent ethyl methacrylate; a copolymer of 70 weight percent methyl methacrylate and 30 weight percent ethyl methacrylate; a copolymer of 50 weight percent methyl methacrylate and 50 weight percent ethyl methacrylate; a copolymer of 40 weight percent methyl methacrylate and 60 weight percent ethyl methacrylate; a copolymer of 10 weight percent methyl methacrylate and 90 weight percent ethyl methacrylate; a copolymer of 90 weight percent methyl methacrylate and 10 weight percent ortho-chloro-styrene; a copolymer of 70 weight percent methyl methacrylate and 30 weight percent orthochlorostyrene; a copolymer of 50 weight percent methyl methacrylate and 50 weight percent ortho-chlorostyrene; a copolymer of 10 weight percent methyl methacrylate and 90 weight percent orthochlorostyrene; polyorthochlorostyrene; polyvinylbenzyl chloride; a copolymer of 70 weight percent acrylonitrile and 30 weight percent vinylidene chloride; a copolymer of equal portions of acrylonitrile and vinylidene chloride; a copolymer of 90 weight percent methyl methacrylate and 10 weight percent acrylonitrile; a copolymer of 50 weight percent methyl methacrylate and 50 weight percent acrylonitrile; a copolymer of 70 weight percent methyl methacrylate and 30 percent by weight para-tert.-butyl-styrene; a copolymer of 80 weight percent methyl methacrylate and 20 weight percent vinyl acetate; a copolymer of 90 weight percent methyl methacrylate and 10 weight percent butyl acrylate; a copolymer of 98 weight percent styrene and 2 weight percent methacrylic acid; a copolymer of 83 weight percent styrene 2 weight percent methacrylic acid and 15 weight percent of vinylbenzyl chloride and a copolymer of 91 weight percent vinylidene chloride and 9 weight percent acrylonitrile.

Papers prepared in accordance with the invention employing synthetic, thermoplastic polymer particles emboss readily with relatively low pressure. Exceptionally desirable embossed papers are obtained wherein the embossed area of the paper is embossed at a temperature about or above the softening temperature of the thermoplastic polymer particles.

Data in the following Tables represent the typical papers obtainable as hand sheets prepared as hereinbefore described.

TABLE IV

Treatment	Control	5% 34CR8*	10% 34CR8*	5% 579*	10% 579*
Retained Microspheres Weight percent	—	2.4	5.0	2.2	5.4
Basis Weight, g/m²	118.4	124.5	128.7	125.6	128.7
Caliper, inches	0.0070	0.0082	0.0093	0.0109	0.0152
Bulk, cc/gm	1.51	1.66	1.84	2.19	3.00
% increase over control	—	10	22	45	99
Taber Stiffness	1.09	1.44	1.83	2.28	4.03
% increase over control	—	30.3	67.9	109.2	269.7
Gurley Stiffness	1.79	2.25	3.12	3.84	6.22
% increase over conttol	—	25.7	74.9	114.5	247.5
Ring Crush, 50 Relative Humidity	21.70	24.19	25.68	31.19	38.08
% increase over control	—	11.4	18.3	43.7	75.4
Ring Crush, high humidity	16.55	18.19	21.01	21.99	24.86
% increase over control	—	9.9	26.9	32.3	50.2
Modulus of Elasticity × 10^4	55.7	46.6	39.9	31.4	20.2
Tensile, p.s.i.	4614	3997	3401	2869	1966
Tensile, breaking length meters	4869	4667	4338	4422	3934

* 579 = polymethyl methacrylate spheres 20 microns average diameter and having a bulk density of 0.6 pound per cubic foot (9.6 gms/l.)

x 34CR8 = spheres of a similar polymer to 579 having average diameters of 10 microns and a density of 4.3 pounds per cubic foot (68.8 gm/l.)

TABLE V

Treatment	Control	5% 34CR8	10% 34CR8	5% 579	10% 579
Stiffness calculated from M.O.E.* $D = EI^{**}$ ($\times 10^4$) Where $I = \frac{bh^3}{12}$	159	214	267	339	591
% Increase over control		35	68	113	272
Stiffness calculated on basis of statement that stiffness increases as square of caliper at constant weight		2.22	2.70	3.88	7.16
% Increase over control		24	51	117	300
***Gurley Stiffness, direct reading	1.79	2.25	3.12	3.84	6.22
% Increase over control		25.7	74.9	114.5	247.5
***Taber stiffness, direct reading	1.09	1.44	1.83	2.28	4.03
% Increase over control		30.3	67.9	109.2	269.7

* M.O.E. = modulus of elasticity = E

**D = stiffness

I = moment of inertia

b = width

h = thickness

*** Gurley stiffness and Taber stiffness (see Pulp and Paper 2nd Edit. 1961, page 1313, Interscience pub.)

WHAT WE CLAIM IS:—

1. A paper comprising a non-woven web of fibers containing enmeshed therein a plurality of synthetic thermoplastic polymer particles each of which is a substantially spherical, hollow particle.

2. A paper as claimed in claim 1 wherein the hollow particles are present in a proportion of from 0.05 to 60 percent of the weight of pulp fibers in the paper.

3. A paper as claimed in claim 1 or 2 wherein the hollow particles have a diameter of from 0.5 to 200 microns.

4. A paper as claimed in any one of claims 1 to 3 wherein the hollow particles have a diameter of from 3 to 50 microns.

5. A paper as claimed in any one of claims 1 to 4 wherein the thermoplastic particles are comprised of a methyl methacrylate polymer.

6. A paper as claimed in claim 1 and substantially as hereinbefore described.

7. A process of making paper which comprises depositing a plurality of fibers upon a screen from an aqueous suspension and subsequently drying and compressing the deposited fibers to form a generally continuous non-woven web, wherein the aqueous suspension from which the fibers are deposited contains a plurality of synthetic, thermoplastic polymer particles each of which is a substantially spherical, hollow particle.

8. A process as claimed in claim 7 wherein the hollow particles have a diameter of from 0.5 to 200 microns.

9. A process as claimed in either one of claims 7 and 8 wherein the hollow thermoplastic polymer particles employed are methyl methacrylate polymer particles.

10. A process as claimed in claim 7 of making paper substantially as hereinbefore described.

11. Paper whenever obtained by the process claimed in any one of claims 7 to 10.

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